

polymer in electrode (I<sub>2</sub>?)

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<p>(54) Title: <b>CELL/MEMBRANE AND ELECTRODE ASSEMBLY FOR ELECTROCHEMICAL CELLS</b></p>		
<p>(57) Abstract</p> <p>The present invention discloses an electrode assembly for use in electrolysis cells in which the catalytic particles (22) forming at least one of the electrodes is in contact with a solid polymer ion exchange material which has a <u>higher equivalent weight than the solid polymer electrolyte membrane (12)</u>. Also disclosed is a method for making the electrode assembly.</p> <div data-bbox="1015 1144 1510 1953"> </div>		

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## Description

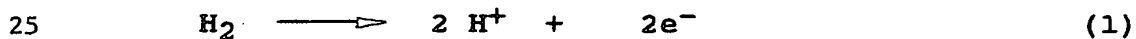
## CELL/MEMBRANE AND ELECTRODE ASSEMBLY FOR ELECTROCHEMICAL CELLS

## Technical Field

5       The technical field to which this invention pertains is an improved electrode assembly for use in electrolytic cells, in particular an electrode assembly for use in fuel cells and electrolysis cells and methods for manufacturing such assembly.

## 10      Background of the Invention

Proton ion exchange membranes used as solid polymer electrolytes in fuel cells and electrolysis cells have been used for years. The preferred electrolyte membranes are those based on perfluorosulfonic acid and  
15      are commercially available as NAFION® from the DuPont de Nemours Company of Delaware. In a typical cell the electrolyte membrane is sandwiched between and in intimate contact with a cathode catalyst and an anode catalyst forming the cathode and anode respectively.  
20      During operation of the cell, reactants are introduced into both the anode and cathode chambers and migrate through the electrodes to the electrolyte membrane/electrode interface where the following half cell reactions take place.



(the direction of the cell reaction is dependent on whether the cell is being operated as a fuel cell or an electrolysis cell.) In either event, one important

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feature of the electrolyte membrane is that it have the requisite ability to transport the ionic species from one electrode to the other electrode easily. This ability is referred to as the resistivity or conductivity of the electrolyte. Since it is important to transport the ionic species across the electrolyte as easily as possible, it is desirable to have an electrolyte membrane having a high conductivity or low resistivity. It is further known that those electrolyte membranes with high conductivity also have, what is termed, a low equivalent weight. The equivalent weight is defined as the weight of polymer in the dry non-hydrated state) per equivalent of conducting ionic species therein. (For fuel cells and electrolysis cells the current conveying ions are protons.) In other words;

Equivalent Weight = polymer molecular weight/No. of equivalents of current conveying ions.

It is believed that the high concentration of proton ions creates a greater number of pathways for the ionic species generated at one electrode to migrate through the electrolyte to the other electrode where the ionic species is catalyzed in the half cell reaction.

In attempting to improve the cell operation, investigators have focused on two aspects of cell technology. First, developing the conductivity of the electrolyte and secondly, improving the catalyst interface at the electrode surface.

As discussed above, the principle interest in electrolyte membrane technology has been to develop membranes having low equivalent weights which therefore have low cell resistivity.

The problems at the electrolyte/electrode interface are more complex. As an example of these problems, this discussion will focus on the operation of a fuel cell; however, similar problems exist in electrolysis cells.

During the operation of the fuel cell, the hydrogen ions formed at the anode/electrolyte interface migrate through the electrolyte membrane to the cathode catalyst. Once they reach the cathode electrode/electrolyte interface, the hydrogen ions must come in contact with a reactive catalytic site on the cathode electrode where, in the presence of the oxidant, the half cell reaction (2) takes place.

In order for the cathode electrode to operate properly, it must possess certain physical properties. It must be gas permeable to permit the oxidant to pass through it to the electrode/electrolyte interface. It must further be electrically conductive and it must permit easy removal of the product water associated with the reaction. Not all of these properties are consistent with one another in the materials used in the preparation of these electrodes. In the prior art electrodes, the catalyst is mixed with a hydrophobic material (TEFLON®), and the mixture is then applied to the surface of the electrolyte membrane and bonded to it through the application of heat and pressure to form the electrode. The theory being that the hydrophobic TEFLON, would prevent the retention of product water while acting as a binder for the catalyst. Unfortunately, TEFLON is not electrically or ionically conductive. This means that in the event the TEFLON surrounds a catalyst particle it would insulate it and remove it as a potential reactive site preventing either electrons or protons from reaching the catalyst particle. Such a result lowers the reactivity and, therefore, the effectiveness of a particular loading of catalyst forming the electrode. This means that in order to compensate for the loss of these reactive sites, and to achieve the desired reactivity for a given electrode, additional catalyst must be loaded onto the electrode. As the preferred catalysts are either noble metal or alloys of noble metals, this adds additional

cost to the manufacture of such devices.

Recently researchers have investigated ways of overcoming the shortcomings of using TEFLON in order to prepare effective electrodes having lower loading of catalyst. One approach is described in Wilson et al, Thin-film catalyst layers for polymer electrolyte fuel cell electrodes, Jour. of App. Electrochem. 22 (1992) pp 1-7 and Wilson et al., High Performance Catalyzed Membranes of Ultra-low Pt Loadings for Polymer Electrolyte Fuel Cells, J. Electrochem Soc. Vol. 139, No 2, February 1992 (the contents of which are incorporated herein by reference). These articles suggest replacing the TEFLON of the prior art with particles of electrolyte membrane material (NAFION). Mixing this NAFION material with the catalyst particles and bonding them to the surface of the electrolyte membrane thereby forming the electrode. In effect since the binder material is the same material as the electrolyte it will have the same ionic electrical conductivity as the electrolyte membrane. And although it does not have the hydrophobicity of the TEFLON, this may be achieved by applying a TEFLON coated, conductive fabric or paper to the back of the electrode at the opposite face from the electrolyte/electrode interface to deal with the problem of water retention.

Although these advances have improved the operation of these cells, further improvements are necessary to lower the cost of these cells and to improve their efficiency.

#### Brief Description of the Invention

The present invention discloses an improved electrode assembly comprising a solid polymer electrolyte membrane positioned between and in contact with a cathode and an anode, wherein the cathode contains catalytic particles in contact with a solid polymer ion exchange material having a higher equivalent

weight than the equivalent weight of the electrolyte membrane.

The present invention further discloses an improved solid polymer electrolyte membrane for use in electrolytic cells (for example fuel cells as well as electrochemical electrolysis cells). The electrolyte comprises an ion exchange membrane material having at least two regions formed of ion exchange polymers, an interior region and an exterior region wherein the exterior region is an ion exchange material having a higher equivalent weight than the ion exchange material of the interior region. And where the exterior region forms at least one surface of the electrolyte membrane.

Also disclosed is an electrode assembly for use in electrolytic cells having an anode catalyst bonded to one surface of the solid polymer electrolyte as described above and a cathode catalyst bonded to the opposite side of the electrolyte from the anode catalyst, where the cathode particles are in intimate contact with the exterior region of the electrolyte membrane.

Still a further feature of the invention is an electrode assembly for use in electrolytic cells in which the cathode electrode is in intimate contact with the surface of the electrolyte membrane of uniform equivalent weight and comprises a mixture of catalytic particles and proton ion exchange material, said proton ion exchange material having a higher equivalent weight than the electrolyte membrane. and having an anode electrode in intimate contact with the opposite surface of the electrolyte membrane from the cathode electrode.

Further disclosed is a method of manufacturing an electrode assembly of the present invention and a electrolytic cell utilizing such an assembly.

Still further, is disclosed a fuel cell utilizing the electrode assembly of the present invention.

### Brief Description the Drawings

Figure 1 is a cross-sectional view of ne embodiment of an electrode assembly of the present invention.

5 Figure 2 is a graph depicting how the activity for oxygen reduction of a platinum catalyst changes with the concentration of sulfonic acid groups in a solution of trifluoromethane sulfonic acid. And shows similar behavior of platinum catalyst on a NAFION membrane.

10 Figure 3 is a graph depicting the oxygen reduction activity of a platinum catalyst on a NAFION membrane at differing states of hydration (different effective equivalent weights).

### Best Mode for Practicing the Invention

15 Referring to Figure 1, the electrode assembly 10 of the present invention comprises an ion exchange polymer electrolyte membrane 12 having an anode electrode 14 on one surface 16 of the electrolyte membrane 12 and a cathode electrode 18 on the surface 20 of the  
20 electrolyte membrane 12 opposite the surface 16 on which the anode 14 is affixed, wherein the cathode catalyst particles 22 are in intimate contact with an ion exchange material having a higher equivalent weight than the electrolyte membrane 12.

25 The ion exchange membranes useful as the electrolyte membrane maybe any of the conventional solid polymer membranes used as a solid polymer electrolyte in prior art electrolytic cells. The preferred polymer membranes are proton ion exchange membranes and are  
30 members of the NAFION® family of perfluorosulfonic acid polymers manufactured by DuPont de Nemours Company of Delaware. As was discussed above, the equivalent molecular weight of electrolyte membrane is important in selecting a membrane which will have the necessary high  
35 conductivity or low resistivity to be useful in the operation of the cell. Membranes having equivalent



molecular weights of between about 800 and about 1200 are preferred and the most preferred membrane is NAFION 117 which has an equivalent molecular weight of 1100.

The materials for forming the anode are also  
5 conventional and would be manufactured and bonded to the electrolyte membrane in conventional manner. Typically, this would comprise forming a mixture of anode catalytic particles and a binder (typically TEFLON®) and then applying this mixture or paste onto the surface of the  
10 electrolyte and then bonding and forming the anode through the application of heat and pressure.

The cathode electrode for use in the electrode assembly may be formed by forming a mixture or suspension of catalytic particles at the desired loading  
15 with particles of a proton ion exchange polymer material which acts as a binder where the polymer has an equivalent molecular weight higher than that of the electrolyte membrane. This ion exchange material may be a perfluorosulfonic acid type material such as NAFION  
20 117 or other material which is either based on the same base polymer as that of the electrolyte membrane or a different polymer while the catalytic particles may be those conventional catalyst materials used in this art. The key feature in selecting the ion exchange polymer  
25 material is that it has an equivalent molecular weight greater than that of the electrolyte membrane. The mixture or suspension is then applied to the surface of the electrolyte membrane in a uniform thickness and through the application of heat and pressure caused to  
30 bond to the surface of the electrolyte membrane. The concentration of polymer to catalyst material will vary depending on the materials used and the cell design, however, it is believed that concentrations of about 20 wt % to about 40 wt% polymer to catalyst be preferred,  
35 and is preferably substantially uniformly distributed throughout the ion exchange material.

In forming the cathode electrode on the surface of

the electrolyte membrane, it is desirable to make the cathode electrode at least coextensive with the electrolyte surface which is to come in contact with the oxidizing material. This will permit optimum reactivity for the electrode assembly as the higher reactivity for the cathode catalyst, due to its contact with the exterior region of the electrolyte membrane, will be at its maximum.

Alternate manufacturing approaches would be to cast a mixture or suspension of the high equivalent weight material and the catalyst particles onto a non-bonding surface to form a smooth, uniform thickness film. Cause the film to dry and then remove the film from the surface and place it in contact with the surface of the electrolyte. Then bond the film to the electrolyte surface through heat and pressure.

Naturally, it is contemplated that either an anode electrode or a cathode electrode may be prepared by any of these processes.

A further variation for manufacturing such electrodes, would be to prepare a suspension or mixture of the ion exchange polymer of a higher equivalent weight than the electrode membrane material together with the desired catalytic particles and paint or spray the suspension or mixture onto the surface of the electrolyte material to a desired thickness. Then drying the suspension and bonding the electrode through the application of heat and pressure.

An alternate approach to manufacturing the electrode assemblies of the present invention would be to prepare an ion exchange electrolyte membrane useful in practicing this invention is comprised of two regions formed of ion exchange polymers having different equivalent weights. The electrolyte membrane would have an interior region and an exterior region where the interior region is comprised of an ion exchange electrolyte material having a lower equivalent weight

than the exterior region and where the exterior region forms at least on of the major surfaces of electrolyte membrane to which at least one of the electrodes is bonded, preferably the cathode.

5 The ion exchange membrane used to form both the exterior region and the interior region of the electrolyte could be the same polymer family as described above for the electrolyte membrane i.e. a member of the perfluorosulfonic family. However, the  
10 polymer selected for the exterior region must have a higher equivalent weight than that of the interior electrolyte membrane. In the case where the preferred electrolyte, NAFION 117, is used as the interior  
15 membrane, the exterior membrane would have an equivalent weight greater than 1100. However, other ion exchange polymers which would operate as electrolytes in these electrolytic processes and which have equivalent weights greater than that of the interior electrolyte membrane would also be useful.

20 The thickness of the overall electrolyte membrane will be conventional for electrolysis cells which is typically about 2 mils to about 10 mils. The thickness of the exterior region will be about the same thickness as the prior art bonded cathodes used in solid polymer  
25 electrolyte electrolysis cells. Typically, this will be about 0.5 mils to about 2 mils. However, the design criteria for selecting a particular membrane will vary with a particular cell design or electrolyte used and are known to those skilled in this art.

30 As in the previous method of forming the electrolyte assembly, it is desirable to make the electrode at least coextensive with the surface of the electrolyte to be exposed to the oxidizing fluid.

35 Such exterior regions having the higher equivalent weight than the interior electrolyte may be formed in a number of ways. One method is to bond a layer of a first ion exchange membrane onto the surface of a second ion

exchange membrane where the first ion exchange membrane has an equivalent weight higher than that of the second ion exchange membrane and the first ion exchange membrane forms the exterior region of the electrolyte membrane. This could be achieved by merely selecting the desired electrolyte membranes, at the predetermined thickness, forming a layer with the two membranes and then bonding them to form a unitary electrolyte. It is contemplated that the laminate bonding could be achieved through the application of pressure and heat, the parameters of which would be the same as those used to bond the electrodes to the surfaces of the electrolyte of the prior art.

In this format, the formation of the anode and the cathode onto the electrolyte to form the electrode assembly would be performed using conventional techniques. This would include applying catalyst particles to opposite surfaces of the electrolyte membrane (the cathode catalyst being deposited onto the surface of the exterior region of the electrolyte membrane) and formed into anode and cathode electrodes through the application of heat and pressure. The respective loadings of catalyst to form the anode and cathode may be conventional; however, it is contemplated that in view of the improved reactivity of the cathode catalyst in contact with the exterior region of the electrolyte membrane, less catalytic material will be needed to achieve the same cell performance.

It is believed that by creating the electrodes with the catalyst material in intimate contact with the high equivalent weight polymer that improved catalytic activity will result. This is based on results of certain experiments which reveal that the oxidation reduction activity of platinum catalysts is increased as the concentration of acid anion groups and accompanying proton ions is decreased within the polymer material.

Such a relationship may be deduced from the results

of the experiments shown in the Figures. In Figure 2, the oxygen reduction activity of platinum was plotted against the concentration of acid groups, in this case sulfonic acid groups, in a solution of liquid trifluoromethane. As is self-evident from the graph, the oxygen reduction activity of the catalyst is inversely proportional to the concentration of sulfonic acid groups. What is additionally noteworthy about this finding is that the oxygen reduction activity of a conventional electrolyte membrane formed of NAFION 117, having an equivalent weight of 1100, with a platinum catalyst bonded to opposite surfaces to act as an anode and cathode, has the same oxygen reactivity at the same concentration of sulfonic acid groups in the membrane as in the liquid solution, confirming the results of the liquid experience.

Further evidence of the relationship between the concentration of acid groups in the membrane material and the oxygen reactivity of the catalyst is demonstrated in Figure 3, in which the effective concentration of acid groups is varied through hydration or dehydration of the membrane. In essence, this simulates how the equivalent weight of a polymer would affect the oxygen reduction activity of the catalyst if one assumes that the equivalent weight is directly proportional to the concentration of acid groups. In this graph, an electrolyte membrane formed of NAFION 117 and platinum electrodes was operated in a fuel cell in which the relative humidity of the fuel (hydrogen gas) was varied during operation. It is believed that as the humidity of the fuel is varied, the hydration of the membrane varies, which in turn varies the effective concentration of the acid groups in the polymer. As can be seen, the greater the hydration the lower the oxygen reactivity of the cell. In each of these experiments, it is clear that the higher the equivalent molecular weight the greater the oxygen reactivity.

Th resulting electro~~d~~ assembly would then b  
placed in a conventional fu~~l~~ cell or electrolysis cell  
assembly to form the fuel cell or electrolysis cell  
having improved properties. Such a cell would have a  
5 porous hydrophobic paper positioned in contact with the  
surface of the cathode opposite the cathode/electrolyte  
interface, means for supplying a fuel to the anode and  
an oxidant to the cathode, all of which are known and  
conventional. Such an electrolytic cell would have  
10 ~~improved oxidation reactivity of the cathode electrode~~  
without any meaningful loss of cell conductivity. This  
will result in higher performance from the cell.

By creating electrode assemblies of the present  
invention, the efficiency of the devices in which they  
15 operate will be enhanced as the activity of the  
catalysts will be improved while maintaining the high  
specific conductance of the electrolyte.

## CLAIMS

1. An improved fuel cell electrode assembly comprising a solid polymer electrolyte membrane positioned between and in contact with an anode and a cathode where said cathode contains a catalytic material which is in  
5 contact with a solid polymer ion exchange material having a higher equivalent weight than the electrolyte membrane.
2. The electrode assembly of claim 1 wherein the cathode catalytic material is dispersed substantially uniformly throughout the ion exchange material.
3. The electrode assembly of claim 1, wherein the solid polymer ion exchange material is in the form of a layer having a thickness of about 2 mils to about 10 mils.
4. An electrode assembly for use in fuel cells, said electrode assembly comprising a ion exchange solid polymer electrolyte, positioned between and in contact with an anode electrode and a cathode electrode wherein  
5 said electrolyte comprises an interior region and an exterior region in which the ion exchange solid polymer electrolyte of said exterior region has a higher equivalent weight than the ion exchange solid polymer electrolyte of the interior region and said cathode is  
10 in intimate contact with said exterior region.
5. The electrolyte of claim 4 wherein the ion exchange polymer of the interior and exterior regions is a perfluorosulfonic acid.
6. An electrode assembly for use in electrochemical fuel cells or electrochemical electrolysis cells said electrode assembly having a solid polymer electrolyte membrane having two surfaces wherein on one surface is

5 bonded a catalytic material to form the cathode where a cathode catalyst is in contact with an ion exchange material having a higher equivalent weight than the electrolyte membrane.

7. The electrode assembly of claim 6 wherein the catalytic material of the cathode is substantially uniformly dispersed in the ion exchange polymer having a higher equivalent weight than the polymer electrolyte.

8. A method of making an electrolyte assembly having uses in a electrolytic cell comprising a solid polymer electrolyte membrane having, on opposite sides of said electrolyte membrane, an anode and a cathode each in  
5 intimate contact with the surface of the electrolyte comprising

forming a mixture of the cathode catalyst and particles of a solid polymer ion exchange material having an equivalent weight higher than that of the  
10 solid polymer electrolyte;

curing the mixture of the catalyst and the ion exchange material to form a cathode;

applying the cathode to the opposite surface of the solid polymer electrolyte from the anode and applying  
15 sufficient pressure and heat to cause the cathode to bond to the surface of the solid polymer electrolyte.

9. The method of claim 8 wherein the cathode for both surfaces are applied and pressure bonded simultaneously.

10. A method of making an electrolyte assembly having uses in electrolytic cells comprising a solid polymer electrolyte membrane having, on opposite sides of said electrolyte membrane, an anode catalyst and a cathode  
5 catalyst in intimate contact with the surface of the electrolyte comprising



applying a layer of ion exchange material to at least one surface of a solid polymer electrolyte wherein the equivalent weight of the ion exchange material is greater than that of the solid polymer electrolyte, bonding said ion exchange material to the surface of the solid polymer electrolyte membrane, applying a catalytic material to the surface of the ion exchange material bonded to the solid polymer electrolyte; and

~~applying sufficient heat and pressure to cause the catalytic material to be embedded into the layer of ion exchange material thereby forming the cathode electrode; and~~

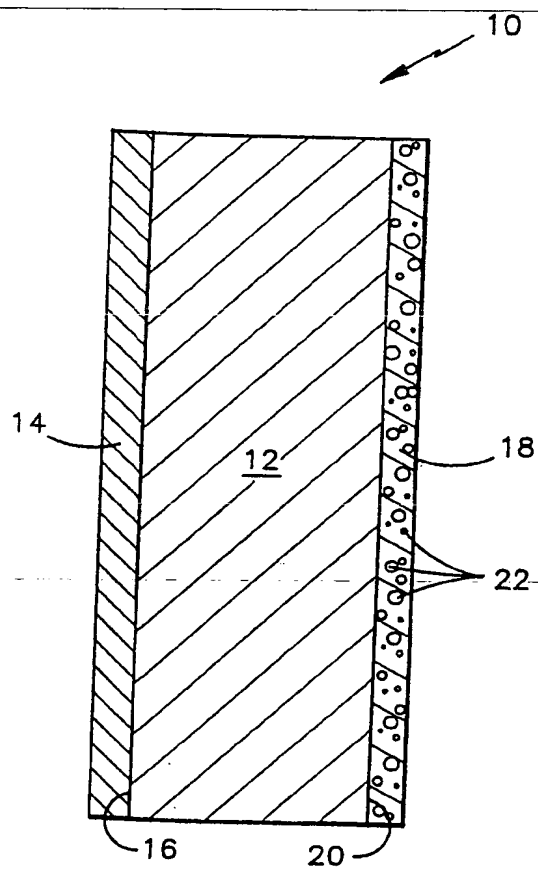
applying a second catalytic material to the opposite surface of the solid polymer electrolyte; and applying sufficient pressure and heat to cause the catalytic material to be embedded into the surface of the solid polymer electrolyte and thereby forming the anode.

11. The method of claim 10 wherein the anode and cathode are bonded simultaneously.

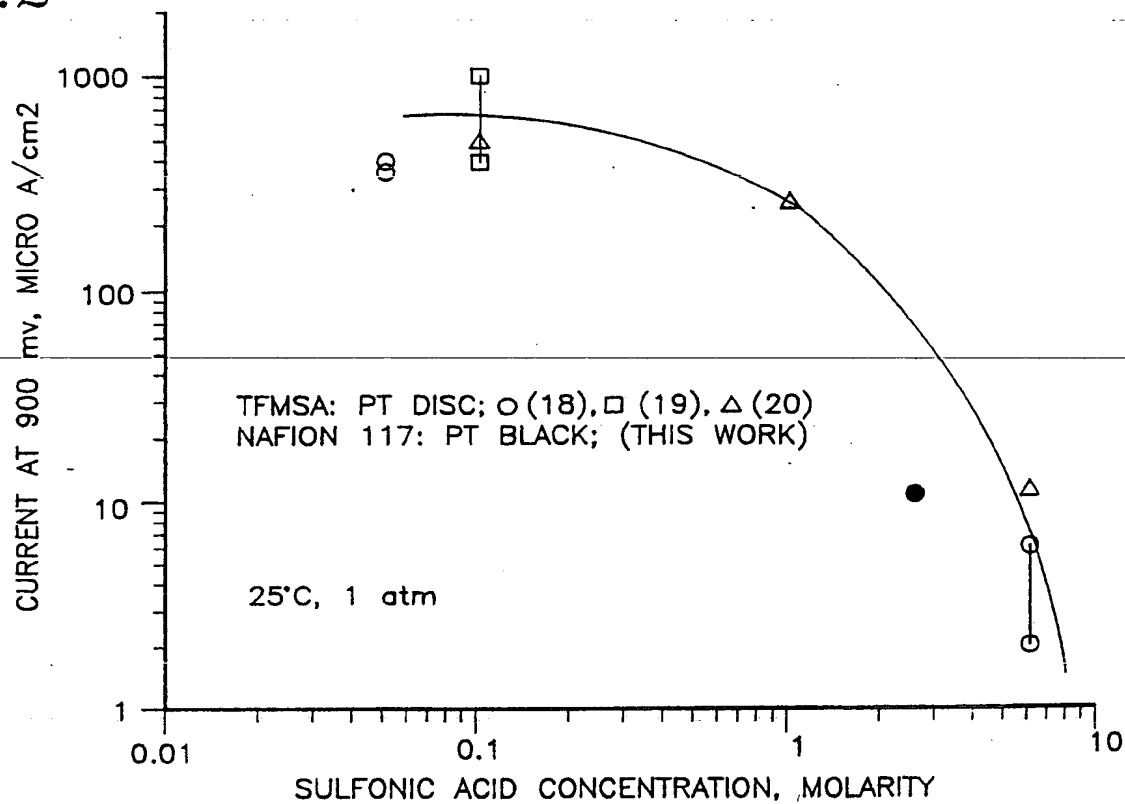
12. The method of claim 10 wherein the catalysts for the anode and the cathode are different.

13. A fuel cell comprising a solid polymer electrolyte membrane, having an anode and cathode positioned on opposite surfaces of the electrolyte where catalytic particles are in intimate contact with an ion exchange polymer having a higher equivalent weight than the electrolyte membrane.

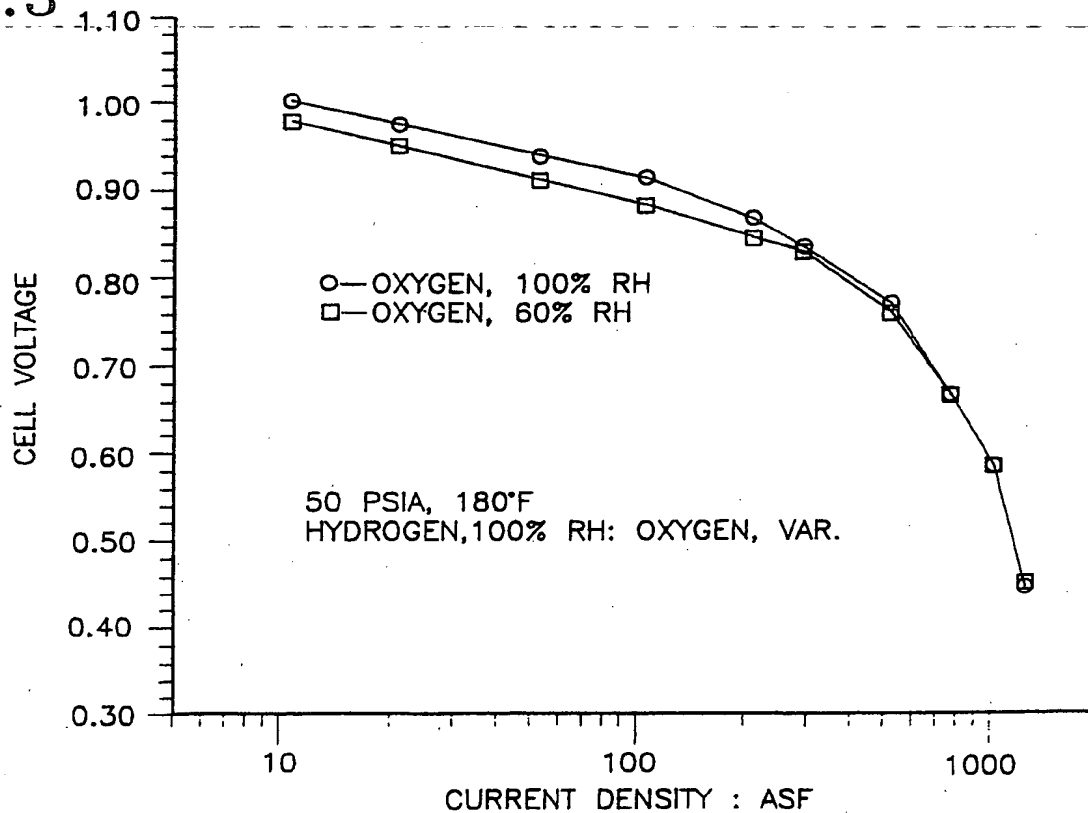
14. The fuel cell of claim 13 wherein the catalytic particles are substantially uniformly dispersed throughout the ion exchange polymer forming the cathode.

*fig. 1*

*fig. 2*



*fig. 3*



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/13620A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01M8/10 C25B9/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF POWER SOURCES, vol. 36, no. 3, 1 December 1991 LAUSANNE CH, pages 299-320, SUPRAMANIAM SRINIVASAN ET AL 'High energy efficiency and high power density proton exchange membrane fuel cells - electrode kinetics and mass transport' see page 306 see page 311, last paragraph see page 302, paragraph 1 see page 301, paragraph 2	1, 2, 6, 7, 13, 14
A	---	8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/13620

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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2	A PROGRESS IN BATTERIES AND SOLAR CELLS, vol. 8, no. 1, 1989 CLEVELAND US, pages 302-305, J.R. HUFF 'THE ION EXCHANGE MEMBRANE ELECTROLYTE FUEL CELL' see page 303, paragraph 2; table I ---	1
1	P,X EP,A,0 577 291 (JOHNSON MATTHEY PLC) 5 January 1994 see column 10, line 16 - line 42 see column 10, line 54 - column 11, line 2 ---	1,2,8,9, 13,14
1	A WO,A,92 15121 (US ENERGY) 3 September 1992 see page 8, line 14 - page 9, line 10; claims 5-7 see page 14, line 32 - page 15, line 14 ---	1,8,9
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Information on patent family members

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